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Dichroism in photoelectron-fluorescence coincidence spectroscopy of rotating linear molecules

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Abstract . This paper investigates dichroic properties of photoelectron-fluorescence coincidence spectroscopy with respect to electromagnetic radiation both absorbed in and emitted from a rotating linear molecule Difference in two functions describing correlation between spin-unresolved angular photocurrent and fluorescence have been studied This difference may correspond to different helicities of circular polarization of either of the absorbed and emitted photon or to two orthogonal linear polarization of fluorescence This dichroism is shown to have properties which are either different from or absent in the corresponding photoelectron as well as fluorescence dichroic spectra observed independently The correlation functions describing dichroic effects are not only simple but also provide an alternative method to extract from experimental measurements the theoretical parameters needed to characterize photoelectron-fluorescence coincidence spectroscopy in rotating linear molecules

Keywords . Circular dichroism ; linear dichroism , Hunds coupling schemes (a) and (b)

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1. Introduction

Angular distribution of spin-unresolved photoelectrons ejected in an electric dipole (E1) approximation from an unoriented and unpolarized atom or molecule is well known to be described by [1]

$$\frac{d\sigma_p(m_r)}{d\hat{k}_p} = \frac{\sigma_p}{4\pi}\left[1+\frac{1}{2}\left(2-3m_r^2\right)\beta_p P_2\left(\cos\theta_p\right)\right]. \tag{1}$$

Here, σ_p and β_p are the integrated photoionization cross-section and angular asymmetry parameter, respectively. The variable m_r in the distribution (1) specifies the state of polarization of the ionizing radiation : $m_r = 0$ for linearly polarized (LP) and $m_r = \pm 1$ for circularly polarized (CP) photons. An unpolarized (UP) electromagnetic wave is considered to be an even mixture of left circularly polarized (LCP, $m_r = -1$) and right circularly polarized (RCP,

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$m_f = \pm 1$) radiation. Further in (1), $\boldsymbol{k}_p\left[k_p, \hat{k}_p(\theta_p, \phi_p)\right]$ is the propagation vector of photoelectron in space (or laboratory)-frame of reference OXYZ centered at 0. The polar OZ axis of this frame is taken to be in the direction of the electric vector of the LP ionizing radiation ; a CP or UP absorbed photon, on the other hand, is considered to be incident along OZ.

Expression (1) is, obviously, not affected by the helicity of the absorbed photon if it is CP. This absence of any difference in the effects produced by the absorption of RCP and LCP radiation [*i.e.*, non-existence of circular dichroism (CD) with respect to the absorbed photon] is a well known property of photoelectron spectroscopy (PES) of unoriented and unpolarized atomic and molecular targets.

It has, on the other hand, been shown by several workers [2-5] that intensity of polarized fluorescence emitted in the spontaneous decay of photoexcited atoms and molecules or of excited photoions of these species can be written as [5]

$$\frac{dI(m_f;\hat{\varepsilon}_d)}{d\omega} = I_0\left\{1 + m_f f_1(J, J_f)\,\alpha_1 \cos\theta_d \sin 2\chi_d + \frac{1}{2}\left(2 - 3m_f^2\right) f_2(J, J_f)\right.$$

$$\left. P_2(\cos\theta_d) - \frac{3}{2}\sin^2\theta_d \cos 2\gamma_d \cos\chi_d\right]\alpha_2\Bigg\}. \qquad (2)$$

In this expression, $\omega_d(\phi_d, \theta_d, \gamma_d)$ are the Euler angles which specify, with respect to the OXYZ coordinate system, orientation of the frame of reference in which fluorescence is detected, *i.e.*, the detector-frame $OX_dY_dZ_d$ which is concentric with respect to the space-frame of reference. $(\cos\chi_d, i\sin\chi_d, 0)$ are the Cartesion components [2-5] of the polarization vector $\hat{\varepsilon}_d$ of fluorescence detected in $OX_dY_dZ_d$ coordinate system. Here, we have, $\chi_d = -\frac{\pi}{4}$ for LCP, $\chi_d = \frac{\pi}{4}$ for RCP, and $\chi_d = 0$ or $\frac{\pi}{2}$ for LP along the OX_d or OY_d axis, respectively. Further in (2), while f_1 and f_2 are two non-dynamical quantities explained further in this paper, both α_1 and α_2 depend upon the dynamics which created photoexcited target or excited photoion of the target whose spontaneous decay emits fluorescence.

The fluorescence intensity measured in (2) is certainly different for the absorption of RCP and LCP radiation. But this CD with respect to the absorbed photon in fluorescence spectroscopy (FS) is present only as long as the emitted radiation too is CP (*i.e.*, $\chi_d = \pm\frac{\pi}{4}$) and is not detected perpendicular ($\theta_d = \frac{\pi}{2}$) to the direction of the incident light. Eq. (2) further reveals that in order to see the difference in the intensities of RCP and LCP fluorescence (*i.e.*, CD with respect to the emitted photon) the absorbed radiation too must not only be CP, but also be incident in directions other than perpendicular to the fluorescence detector. In addition to these, one also learns from eq. (2) that fluorescence polarized linearly in the OX_d ($\chi_d = 0$) and OY_d ($\chi_d = \frac{\pi}{2}$) directions have equal intensities if observed in a direction with either $\theta_d = 0/\pi$ (*i.e.*, along/opposite to the OZ-axis) or $\gamma_d = (2n+1)\frac{\pi}{4}$ with $n = 0 - 3$.

In this paper, we show that all of the above features of PES and FS with respect to the polarization of the absorbed or emitted photons are not only changed but new ones appear in those experiments in which photoelectron and fluorescence produced in two successive steps

are observed simultaneously. For example, in the photoelectron-fluorescence coincidence (PEFCO) spectroscopy, CD with respect to the absorbed photon is present in the simultaneously observed angular photocurrent and CP or LP fluorescence, even if the later is detected in the X-Y plane. Secondly, in a PEFCO experiment, CD with respect to the emitted light exists also for absorbed radiation other than CP. Furthermore, the expression describing correlation [5] between a photoelectron and fluorescence is quite complicated even if one does not analyse spin of the departing electron. It is therefore natural to look for ways in which this expression can be simplified. One of the possibilities to achieve this goal, which has already been explored in Reference [5] is to consider those experimental geometries when contributions of some of the terms in the expression for correlation between a photoelectron and fluorescent photon disappears.

The other straight forward method to simplify a PEFCO expression is to consider a difference of two PEFCO measurements corresponding to different polarizations of the absorbed or emitted light. In such cases, the resulting expressions becomes so simple that one can easily extract theoretical parameters from experimental measurements.

For such convenience and for the physical reasons discussed earlier in this Introduction, we study in PEFCO spectroscopy CD with respect to both absorbed as well as emitted radiations. Needless to say, this CD is nothing but the difference in the measurements of two PEFCO experiments performed with different helicities of CP absorbed or emitted photons. In addition, we also investigate in this paper the advantages of studying difference in two PEFCO spectra corresponding to the same polarization of the absorbed light but fluorescence polarized linearly in two mutually perpendicular directions. Cherepkov and Colleagues [6-8] have, on the other hand, studied difference in the angular distribution of photoelectrons produced in E1 ionization of fixed molecules [7] and polarized linearly in two mutually perpendicular directions.

There have, recently, been several [9-16] studies of non-coincident FS following photoionization in linear molecules belonging to a $C_{\infty v}$ or $D_{\infty h}$ point group. Here one detects only the fluorescence without observing photoelectron emitted in the first of a two step process. In some [13-16] or these experiments performed on N_2 and CO molecules, the fluorescence has even been rotationally resolved.

On the other hand, several groups [17-20] have developed high resolution PES techniques. These developments have made it possible to resolve photoelectrons arising from the production of diatomic ions in different rotational states of H_2^+, N_2^+, O_2^+, *etc.* which have relatively large rotational constants.

These successful non-coincident measurements or rotationally resolved PES [17-20] or of subsequent FS [13-16] for relatively light linear molecules suggest that it should, at least in near future, be possible to perform experiments detecting photoelectron and fluorescence simultaneously. In fact rotationally unresolved photoelectron-fluorescence coincident (PEFCO) spectroscopy has already been carried out by Smith *et al* [21] for CF_4, SiF_4, $SiCl_4$ and $GeCl_4$, but considering neither the spin-selection for angular distribution of photoelectrons nor polarization of FS.

In this paper, we therefore report probably the first study of dichroic effects in PEFCO spectroscopy of linear molecules. We consider molecule to be rotating according to Hund's

coupling scheme [22-24] either (a) or (b). Using wave functions of definite parity [25] to properly describe rotation of a linear molecule, we present in the Section 2 a general expression which is applicable to PEFCO spectroscopy in Hund's scheme (a) as well as (b). This expression is used to derive in the Section 3 general relations describing various dichroic effects in PEFCO spectroscopy of rotating linear molecules. Properties of these effects are also discussed therein. Section 4 presents an application of the theoretical framework developed herein with the final Section 5 containing conclusions.

2. Theory

Let us consider angular distribution of photoelectrons e_p emitted in

$$h\nu_0 + AB(J_0 M_0 p_0) \rightarrow AB^{+*}(JMp) + e_p(\boldsymbol{k}_p) \tag{3a}$$

and observed alongwith the photon of frequency ν coming out in the successive process

$$AB^{+*}(JMp) \rightarrow AB^{+}\left(J_f M_f p_f\right) + h\nu . \tag{3b}$$

In (3), AB^+ is the residual molecular ion left after spontaneous radiative decay of the excited photoion AB^{+*} formed after the ejection of e_p due to absorption of a photon of frequency ν_0 in the target molecule AB. All of the AB, AB^{+*}, and AB^{++} are linear molecules belonging to either of the $C_{\infty v}$ or $D_{\infty h}$ point groups. Rotation of these three molecular species has been taken into account so that $\left|J_0 M_0 p_0\right\rangle$ $|JMp\rangle$, and $\left|J_f M_f p_f\right\rangle$ in (3) are their respective parity adapted [25] states in Hund's coupling scheme [22-24] either (a) or (b). (J_0 , J, J_f) are the total angular momenta of these states, (M_0, M, M_f) are the respective projections of these angular momenta on OZ quantization axis of the space-frame, and (p_0, p, p_f) are the parities of the three states of (AB, AB^{+*}, AB^+) respectively. Further in (3a), photoelectron is ejected with energy $\varepsilon_p = \hbar^2 k_p^2 / 2m = (E_0 + h\nu_0) - E$ where E_0 and E are the energies of AB and AB^{+*} respectively. If E_f is the energy of $A\,B^+$, then emitted fluorescence has frequency $\nu = (E - E_f)/h$.

Cross section for the two successive processes (3), observed simultaneously, is given by [5]

$$\frac{d^2\sigma_{fp}\left(m_r;\hat{\varepsilon}_d\right)}{d\hat{k}_p d\omega_d} = \sum_{KQQ'} E_Q^K \cdot \mathcal{D}_{Q'Q}^{K}\left(\omega_d\right) C_{KQ}^{(1)}\left(J;m_r;\boldsymbol{k}_p\right). \tag{4}$$

Here $\mathcal{D}$'s are the rotational harmonics [26] and the coefficient C's are defined by

$$C_{KQ}^{(1)}\left(J;m_r;\boldsymbol{k}_p\right) = (-1)^{-J-J_f} 3(2J+1) I_0 \begin{Bmatrix} 1 & 1 & K \\ J & J & J_f \end{Bmatrix} \left\langle T\left(J;m_r;\boldsymbol{k}_p\right)^{+}_{KQ} \right\rangle, \tag{5a}$$

or

$$C_{KQ}^{(2)}\left(J;m_r;\boldsymbol{k}_p\right) = (-1)^{-J-J_f} 3 I_0 \begin{Bmatrix} 1 & 1 & K \\ J & J & J_f \end{Bmatrix} \rho_{KQ}\left(J;m_r;\boldsymbol{k}_p\right) d\sigma_p\left(J;m_r;\boldsymbol{k}_p\right). \tag{5b}$$

In (5), $\left\langle T\left(J;m_r;\boldsymbol{k}_p\right)^{+}_{KQ}\right\rangle$ is the state multipole [27], and $\rho_{KQ}\left(J;m_r;\boldsymbol{k}_p\right)$ is the normalized statistical tensor [27], and $d\sigma_p\left(J;m_r;\boldsymbol{k}_p\right)$ is the differential cross section (1) for the photoionization process (3a). These three quantities are taken from the respective eqs. (I.A11) [28], (I.A12a), and (I.12b) for Hund's scheme (a) ; whereas, for case (b), the corresponding expressions for the three quantities are obtained from the Appendix B in Reference [28].

Further in (4) $E^{K}_{Q}\left(\hat{\varepsilon}_d,\hat{\varepsilon}^{*}_d\right)$ are the components of a tensor of rank two describing polarization of the emitted fluorescence in detector frame $OX_dY_dZ_d$. These components are given by

$$E^{0}_{0}=-\frac{1}{\sqrt{3}};\ E^{1}_{0}=\frac{1}{\sqrt{2}}\sin 2\chi_d;\ E^{2}_{0}=-\frac{1}{\sqrt{6}};\ E^{2}_{\pm 2}=\frac{1}{2}\cos 2\chi_d;\ E^{1}_{\pm 1},E^{2}_{\pm 1}=0. \quad (6a)$$

Here, the angle χ_d is the same as that used in Eq. (2). It is obvious from the 6-j symbol present in (5) and from expression (I.A11) that the orders of the multipoles which can contribute to (4) are given by Min $\left(2,2J,2\left(l_p\right)_{max}+3\right)$, where $\left(l_p\right)_{max}$ is the highest partial wave used to represent the photoelectron e_p in (3a). The smallest value which $\left(l_p\right)_{max}$ can take is zero, we therefore have

$$0\le K\le Min(2,2J). \quad (6b)$$

Also, on account of the hermiticity [27] of boh the state multipoles and normalized statistical tensors, present in (5), the coefficient C's too are hermitian, *i.e.*,

$$C^{(i)*}_{KQ}\left(J;m_r;\boldsymbol{k}_p\right)=(-1)^{Q}\,C^{(i)}_{K\bar{Q}}\left(J;m_r;\boldsymbol{k}_p\right). \quad (6c)$$

Studies of dichroism in PEFCO spectroscopy with respect to absorbed or emitted radiation will become simpler if (4) is expanded in two alternative forms. Use of the properties (6a, b) shows that

$$\frac{d^2\sigma_{fp}\left(m_r;\hat{\varepsilon}_d\right)}{d\hat{k}_p d\omega_d}=-\frac{1}{\sqrt{3}}C^{(i)}_{00}+\frac{1}{\sqrt{2}}\sum_{Q}\left\{\mathscr{D}^{1}_{0Q}\left(\omega_d\right)C^{(i)}_{1Q}\sin 2\chi_d\right.$$

$$\left.-\frac{1}{\sqrt{3}}\left[\mathscr{D}^{2}_{0Q}\left(\omega_d\right)-\sqrt{\frac{3}{2}}\left(\mathscr{D}^{2}_{-2Q}+\mathscr{D}^{2}_{2Q}\right)C^{(i)}_{2Q}\cos 2\chi_d\right.\right. \quad (7)$$

In order to obtain second form of this expansion, we note that in expressions (I.A11) for state multipoles $\left\langle T\left(J;m_r;\boldsymbol{k}_p\right)^{+}_{KQ}\right\rangle$, $0\le L_r\le 2$ plus $L_r-K\le L_p\le L_r+K$ with the additional conditions that L_p must be even because (l_p,l'_p) have same parities [28] and K is never allowed to become more than two on account of the inequality (6b). It means, each of the multipoles may have upto Y^{0}_{0}, Y^{Q}_{2} and Y^{Q}_{4}, with $|Q|\le 2$, spherical harmonics contributing to it. One can, therefore, write (4) in the following form as well

$$\frac{d^2\sigma_{fp}(m_r;\hat{\varepsilon}_d)}{d\hat{k}_p d\omega_d} = \frac{I_0\sigma_p}{4\pi}\left\{1+\frac{1}{2}(2-3m_r^2)\beta_p P_2(\cos\theta_p)+\left[m_r f_1(J,J_f)\alpha_1\cos\theta_d \sin 2\chi_a\right.\right.$$

$$+\frac{1}{2}(2-3m_r^2)f_2(J,J_f)\left(P_2(\cos\theta_p)-\frac{3}{2}\sin^2\theta_d\cos 2\gamma_d\cos 2\chi_d\right)\alpha_2\Big]$$

$$+a_2 f_2(J,J_f)\beta_2+m_r\left[a_{11}f_1(J,J_f)\beta_{11}+a_{21}f_2(J,J_f)\beta_{21}\right]+\frac{1}{2}(2-3m_r^2)$$

$$\left.\left[a_{12}f_1(J,J_f)\beta_{12}-(a_{22}\beta_{22}+a_{23}\beta_{23})f_2(J,J_f)\right]\right\}. \qquad (8)$$

This expression contains two non-geometrical and non-dynamical factors $\left[f_1(J,J_f)\right.$ and $\left.f_2(J,J_f)\right]$ which involve only the total angular momenta J of AB^{+*} and J_f of AB^{+}, six geometrical constants (a_{11}, a_{12}, a_2, a_{21}, a_{22}, a_{23}) which are completely determined by the geometry of a PEFCO experiment, and eleven dynamical parameters $(I_0, \sigma_p, \beta_p, \alpha_1, \alpha_2, \beta_{11}, \beta_{12}, \beta_2, \beta_{21}, \beta_{22}, \beta_{23})$. The total fluorescence intensity I_0, among these parameters, depends upon the decay process (3b) ; whereas remaining ten parameters contain amplitude for the photoionization (3a). Expressions for these quantities, which will be useful in the present and future PEFCO studies in rotating linear molecules, are given in eqs. (A1) – (A18) in the Appendix A to this paper.

On comparing with eqs. (1) and (2), we find that the first, second, and the terms enclosed in the first square bracket on the right hand side of (8) represent photoelectron angular distribution and polarized fluorescence, both observed independently in two non-coincident experiments. The remaining terms in (8), therefore, are the contributions to a PEFCO spectrum due to photoelectron-fluorescence correlation when the two are being observed simultaneously. Thus $(\beta_{11}, \beta_{12}, \beta_2, \beta_{21}, \beta_{22}, \beta_{23})$ describe interference between the directions of propagation of photoelectron and of fluorescence in a PEFCO experiment. Although, parameters (σ_p, β_p) and $(I_0, \alpha_1, \alpha_2)$ can be readily extracted from the respective non-coincident measurements of PES and FS, determination of the remaining parameters is, however, difficult from a single eq. (8). In the following we show that $(\beta_{11}, \beta_{12}, \beta_2, \beta_{21}, \beta_{22}, \beta_{23})$ can be readily extracted by measuring dichroism in PEFCO spectroscopy.

3. Dichroism in PEFCO spectroscopy

3.1. CD with respect to absorbed photon :

It is defined by

$$\frac{d^2\sigma_{CD}(\hat{\varepsilon}_d)}{dk_p d\omega_d} = \frac{d^2\sigma_{fp}(m_r=+1,\hat{\varepsilon}_d)}{dk_p d\omega_d} - \frac{d^2\sigma_{fp}(m_r=-1,\hat{\varepsilon}_d)}{d\hat{k}_p d\omega_d}.$$

On substituting (8), we find

$$\frac{d^2\sigma_{CD}(\hat{\varepsilon}_d)}{d\hat{k}_p d\omega_d} = \frac{I_0\sigma_p}{2\pi}\left[(a_{11}\beta_{11} + \alpha_1 \cos\theta_d \sin 2\chi_d) f_1(J, J_f) a_{21}\beta_{21} f_2(J, J_f)\right]. \quad (9)$$

Thus, out of the ten parameters $(\sigma_p, \beta_p, \alpha_1, \alpha_2, \beta_{11}, \beta_{12}, \beta_2, \beta_{21}, \beta_{22}, \beta_{23})$ which are present in the general expression (8), only four $(\sigma_p, \alpha_1, \beta_{11}, \beta_{21},)$ contribute to the CD with respect to absorbed photon in PEFCO spectroscopy. It is obvious from the expressions given in the Appendix A to this paper that coefficients $f_1(J, J_f)$, $f_2(J, J_f)$, a_{11}, a_{21} and parameters $(\alpha_1, \beta_{11}, \beta_{21})$ vanish identically only in certain special cases. Consequently, CD (9) must in general exist in PEFCO spectroscopy. This expression can readily be shown to have following properties :

(i) We have seen from eq. (2) that only a single term containing the parameter α_1 contributes to this CD in non-coincident FS. Although, this term is present also in the expression (9), two additional terms consisting of parameters β_{11} and β_{21} too contribute to the CD (9) in PEFCO spectroscopy. These terms obviously arise from interference between photoelectron and flourescent photon.

(ii) In order to observe CD in case of (2), it is necessary that the detected photon be CP (*i.e.*, $\chi_d = \pm \pi/4$). But we find from eqs. (A3) and (A6) that a_{11} ($\chi_d = 0, \pi/2$) = 0 and $a_{21}(\chi_d = 0, \pi/2) \neq 0$, respectively. Therefore, CD in PEFCO spectroscopy may be present in the detection of even LP fluorescence. It is due to the non-vanishing third term proportional to the parameter β_{21} occurring in (9). Thus measurements of CD (9) in LP fluorescence in a PEFCO experiment can be used to extract parameter β_{21} present in (8).

(iii) CD with respect to the absorbed photon in non-coincident FS vanishes when fluorescence is detected perpendicular ($\theta_d = \pi/2$) to the ionizing radiation. But in case of PEFCO experiments, $a_{11}(\theta_d = \pi/2) \neq 0$ and $a_{21}(\theta_d = \pi/2) \neq 0$. Therefore one can always observe CD (9) even in the X-Y plane. This experimental geometry too is, thus, sufficient to measure the parameter β_{21} needed in the specifications of the PEFCO spectrum (8).

(iv) If the photoelectron is observed along the OZ-axis (*i.e.* $\theta_p = 0$), then (9) reduces to

$$\frac{d\sigma_{CD}(\hat{\varepsilon}_d)}{d\theta_d} = \frac{d^2\sigma_{CD}(\hat{\varepsilon}_d)}{d\hat{k}_p d\omega_d}_{\theta_p=0} \quad \frac{I_0\sigma_p}{2\pi}(\alpha_1 + \beta_{11}) f_1(J, J_f)\cos\theta_d \sin 2\chi_d \quad (10)$$

which vanishes for CP fluorescence observed in X-Y plane or LP fluorescence detected in any experimental geometry. If α_1 has been extracted from non-coincident FS, then a single PEFCO measurement will be sufficient to find the value of β_{11} from (10).

(v) Let us observe photoelectron and fluorescence in the same plane, *i.e.*, $\phi_d = \phi_p$. CD (9) for this geometry becomes

$$\frac{d^2\sigma_{CD}(\hat{\varepsilon}_d)}{dk_p d\omega_d} = \frac{I_0\sigma_p}{2\pi}\Big\{(\alpha_1\cos\theta_d + \Big[P_2(\cos\theta_p)\cos\theta_d$$

$$+\frac{1}{2}P_2^1(\cos\theta_p)\sin\theta_d\Big]\beta_{11}\Big)\times f_1(J,J_f)\sin 2\chi_d + \frac{5}{4\sqrt{6}}\Big[P_2^1(\cos\theta_p)\sin\theta_a$$

$$-P_2^2(\cos\theta_p)\cos\theta_d\Big]\beta_{21}f_2(J,J_f)\sin 2\gamma_d\cos 2\chi_d\Big\}. \qquad (11)$$

That is, CD with respect to absorbed photon exists even in a coplanar geometry consisting of photoelectron and fluorescence detectors plus incident photon beam in a PEFCO experiment in a single plane. This result is opposite to that found in single photoionization [29, 30] of fixed and in double photoionization [31] as well as in photoelectron-Auger electron coincidence spectroscopy [32, 33] of free linear molecules. It was found in References 29-33 that CD does not exist in coplanar experimental configurations. The other property of eq. (11) is that it vanishes neither for CP ($\chi_d = \pm\pi/4$) nor for LP ($\chi_d = 0, \pi/2$) fluorescence.

(vi) Let us assume that photon detector and the fluorescence detector are in the same direction, *i.e.* $\theta_d = \theta_p$ and $\phi_d = \phi_p$. Then one finds from (11) that it becomes identical to (10) which describes CD when photoelectron is observed along the OZ axis whatever may be the location of the fluorescence detector relative to the OXYZ-frame. That is

$$\frac{d\sigma_{CD}^{\uparrow\uparrow}(\hat{\varepsilon}_d)}{d\theta_d} \equiv \frac{d^2\sigma_{CD}(\hat{\varepsilon}_d)}{d\hat{k}_p d\omega_d}\Bigg|_{\substack{\theta_p=\theta_d \\ \phi_p=\phi_d}} = d\sigma_{CD}(\hat{\varepsilon}_d)/d\theta_d. \qquad (12a)$$

On the other hand, if photoelectron and fluorescence are observed in opposite directions, (*i.e.*, $\theta_d = \pi - \theta_p$, $\phi_d = \pi + \phi_p$ then one finds from (9) that

$$\frac{d\sigma_{CD}^{\uparrow\downarrow}(\hat{\varepsilon}_d)}{d\theta_d} = \frac{d^2\sigma_{CD}(\hat{\varepsilon}_d)}{dk_p d\omega_d}\Bigg|_{\substack{\theta_d=\pi-\theta_p \\ \phi_d=\pi+\phi_p}} = -d\sigma_{CD}^{\uparrow\uparrow}(\hat{\varepsilon}_d)/d\theta_d. \qquad (12b)$$

Thus there is an asymmetry in CD (9) in the collinear detector of photoelectron and fluorescence depending upon whether they are observed in the same or opposite direction.

(vii) Parameter α_1 can be determined by measuring CD in non-coincident FS ; β_{11} is extracted by performing of PEFCO measurement in the experimental geometries of either of the eqs. (10) and (12). The remaining parameter β_{21} needed in the complete characterization of the CD (9) with respect to absorbed photon in a PEFCO spectrum is determined from either of the methods discussed in (ii) and (iii) or, alternatively, from eq. (11).

3.2. CD with respect to the fluorescence :

This is defined by

$$\frac{d^2\sigma_{CD}(m_r)}{d\hat{k}_r d\omega_r} \equiv \frac{d^2\sigma_{fp}(m_r;\hat{\varepsilon}_d)}{d\hat{k}_p d\omega_d}\Bigg|_{\chi_d=\pi/4} \qquad \frac{d^2\sigma_{fp}(m_r;\hat{\varepsilon}_d)}{dk_p d\omega_d}\Bigg|_{\chi_d=-\pi/4} \qquad (13)$$

If we look at the expressions (A5) – (A8) for the coefficients a_2, a_{21}, a_{22} and a_{23} respectively, we find that these contain terms which are either independent of χ_d or multiplied by cos 2 χ_d. The contribution of such terms will vanish after (8) is substituted in (13). Consequently, CD with respect to fluorescence in a PEFCO spectrum is given by

$$\frac{d^2\sigma_{CD}(m_r)}{d\hat{k}_p d\omega_d} = \frac{I_0\sigma_p}{2\pi}\left\{\left[\alpha_1\cos\theta_d + \left(P_2(\cos\theta_p)\cos\theta_d + \frac{1}{2}P_2^1(\cos\theta_p)\sin\theta_d\cos\right.\right.\right.$$

$$\left.\left.\left.(\phi_d - \phi_p)\right)\beta_{11}\right]m_r + \frac{1}{2}(2-3m_r^2)P_2^1(\cos\theta_p)\sin\theta_d\sin(\phi_d-\phi_p))\beta_{12}\right\}f_1(J,J_f). \quad (14)$$

According to the Ref. [5], the degree of CP of fluorescence in the present PEFCO study is given by

$$\frac{d^2P_C(m_r)}{d\hat{k}_p d\omega_d} = \frac{d^2\sigma_{CD}(m_r)}{d\hat{k}_p d\omega_d} \Big/ \frac{d^2\sigma_C^+(m_r)}{d\hat{k}_p d\omega_d}. \quad (15a)$$

Here we have defined

$$\frac{d^2\sigma_C^+(m_r)}{d\hat{k}_p d\omega_d} \equiv \left.\frac{d^2\sigma_{fp}(m_r;\varepsilon_d)}{d\hat{k}_p d\omega_d}\right|_{\chi_d=\pi/4} + \left.\frac{d^2\sigma_{fp}(m_r;\varepsilon_d)}{d\hat{k}_p d\omega_d}\right|_{\chi_d=-\pi/4}$$

$$= \frac{I_0\sigma_p}{2\pi}\left\{1 + \frac{1}{2}(2-3m_r^2)\beta_p P_2(\cos\theta_p) + \frac{1}{2}(2-3m_r^2)f_2(J,J_f)P_2(\cos\theta_d)\alpha_2\right.$$

$$+ a_2(\chi_d=\pi/4)\beta_2 + m_r a_{21}(\chi_d=\pi/4)f_2(J,J_f)\beta_{21} + \frac{1}{2}(2-3m_r^2)\left[a_{22}(\chi_d=\pi/4)\beta_{22}\right.$$

$$\left.\left. + a_{23}(\chi_d=\pi/4)\beta_{23}\right]f_2(J,J_f)\right\} \quad (15b)$$

where the second result in (15b) has been arrived at by using expression (8).

Thus the degree (15a) of CP of fluorescence is the normalized CD with respect to the emitted photon. On comparing (14) and (15), we find that the ratios $d^2P_C(m_r)/d\hat{k}_p d\omega_d$ contains more independent parameters than $d^2\sigma_{CD}(m_r)/d\hat{k}_p d\omega_d$.

It will therefore be much easier to extract theoretical parameters from the measurements of unnormalized CD (13). We therefore study in the remaining part of this sub-section some of the properties of (14) which are not evident from a corresponding study of eq. (15).

(i) On comparing (11) and (14), we find that measurement of CD with respect to fluorescence determines an additional parameter β_{12}. The right hand side of (14) becomes identically zero if $\theta_d, \theta_p = \pi/2$, *i.e.*, both of the photoelectron and fluorescence detectors lie in the X-Y plane of the laboratory-frame.

(ii) Expression (14) reduces to

$$\frac{d^2\sigma_{CD}(0)}{d\hat{k}_p d\omega_d} = \frac{I_0\sigma_p}{2\pi} P_2^1(\cos\theta_p)\sin\theta_d \sin(\phi_d - \phi_p) f_1(J, J_f)\beta_{12} \tag{16a}$$

for LP incident light. If the absorbed radiation, on the other hand, is UP, then one finds

$$\frac{d^2\sigma_{CD}(UP)}{d\hat{k}_p d\omega_d} = -\frac{1}{2}\frac{d^2\sigma_{CD}(0)}{d\hat{k}_p d\omega_d}. \tag{16b}$$

(iii) Let us take the detectors for photoelectron and fluorescence in the same plane. Then

$$\left.\frac{d^2\sigma_{CD}(m_r)}{d\hat{k}_p d\omega_d}\right|_{\phi_d=\phi_p} = m_r \frac{I_0\sigma_p}{2\pi}\left[\alpha_1\cos\theta_d + \left(P_2(\cos\theta_p)\cos\theta_d + \frac{1}{2}P_2^1(\cos\theta_p)\sin\theta_d\right)\beta_{11}\right] \times f_1(J, J_f). \tag{17a}$$

For two detectors in the same direction, we get

$$\frac{d^2\sigma_{CD}^{\uparrow\uparrow}(m_r)}{d\hat{k}_p} = m_r \frac{I_0\sigma_p}{2\pi}(\alpha_1 + \beta_{11}) f_1(J, J_f)\cos\theta_p. \tag{17b}$$

If the two detectors, on the other hand, are on opposite directions, then

$$\frac{d^2\sigma_{CD}^{\uparrow\downarrow}(m_r)}{d\hat{k}_p} = -\frac{d^2\sigma_{CD}^{\uparrow\uparrow}(m_r)}{d\hat{k}_p}. \tag{17c}$$

Eqs. (17a-c) reveal that there is no CD with respect to the emitted photon if the experimental geometry is coplanar (consisting of photoelectron and fluorescence detectors in single plane) and the absorbed radiation is either LP or UP.

(iv) The parameters β_{12} can be readily extracted from measurement of (16) in any experimental geometry. For determining β_{11}, (17a) can be used by detecting CP fluorescence in the X-Y plane ($\theta_d = \pi/2$); whereas α_1 is obtained from (17b) or (17c). It is probably needless to remind that, while using (17), the absorbed photon too should be CP.

3.3 Linear dichroism (LD) with respect to fluorescence :

By considering CD with respect to the absorbed photon and with respect to fluorescence, we have so far been able to extract three $(\beta_{11}, \beta_{12}, \beta_{21})$ of the six $(\beta_{11}, \beta_{12}, \beta_2, \beta_{21}, \beta_{22}, \beta_{23})$ interference parameters. In order to determine the remaining three $(\beta_2, \beta_{22}, \beta_{23})$ of these six parameters, let us consider the following difference

$$\frac{d^2\sigma_{LD}(m_r)}{d\hat{k}_p d\omega_d} \equiv \left.\frac{d^2\sigma_{fp}(m_r;\hat{\varepsilon}_d)}{d\hat{k}_p d\omega_d}\right|_{\chi_d=0} - \left.\frac{d^2\sigma_{fp}(m_r;\hat{\varepsilon}_d)}{d\hat{k}_p d\omega_d}\right|_{\chi_d=\pi/2} \tag{18}$$

in the PEFCO spectra for fluorescence polarized linearly in two mutually perpendicular directions along OX_d and OY_d axes, respectively. On substituting (8), one finds that LD with respect to fluorescence in the PEFCO spectrum becomes

$$\frac{d^2\sigma_{LD}(m_r)}{d\hat{k}_p d\omega_d} = \frac{I_0\sigma_p}{4\pi}\left\{b_2\beta_2 + m_r\, b_{21}\,\beta_{21} - \frac{1}{2}\left(2-3m_r^2\right)\left[3\alpha_2 \sin^2\theta_d \cos 2\gamma_d\right.\right.$$

$$\left.\left. + b_{22}\,\beta_{22} + b_{23}\,\beta_{23}\right]\right\} \times f_2\left(J, J_f\right). \tag{19}$$

Here, the new coefficients b_2, b_{21}, b_{22}, and b_{23} have respectively been defined in eqs. (A19)–(A22) in the Appendix A to this paper.

Let us compare (18) with

$$\frac{d^2P_L(m_r)}{d\hat{k}_p d\omega_d} \equiv \frac{d^2\sigma_{LD}(m_r)}{d\hat{k}_p d\omega_d} \Big/ \frac{d^2\sigma_L(m_r)}{d\hat{k}_p d\omega_d}, \tag{20a}$$

where

$$\frac{d^2\sigma_L^+(m_r)}{d\hat{k}_p d\omega_d} \equiv \left.\frac{d^2\sigma_{lp}(m_r, \hat{\varepsilon}_d)}{d\hat{k}_p d\omega_d}\right|_{\chi_d = 0} + \left.\frac{d^2\sigma_{lp}(m_r, \hat{\varepsilon}_d)}{d\hat{k}_p d\omega_d}\right|_{\chi_d = \pi/2}$$

According to Ref. [5], (20a) is the degree of LP of fluorescence in a PEFCO experiment performed without analysing spin of photoelectrons. This also corresponds to the normalized LD with respect to the emitted radiation. Using (8), we find

$$\frac{d^2\sigma_L^+(m_r)}{d\hat{k}_p d\omega_d} = \frac{I_0\sigma_p}{4\pi}\left\{\left(2-3m_r^2\right)\left[\beta_p P_2\left(\cos\theta_p\right) + a_2\, f_2\left(J, J_f\right) P_2\left(\cos\theta_d\right)\right]\right.$$

$$+\left[a_2(\chi_d = 0) a_2(\chi_d = \pi/2)\right]\beta_2\, f_2\left(J, J_f\right) + m_r\left[a_{21}(\chi_d = 0) + a_{21}(\chi_d = \pi/2)\right]$$

$$f_2\left(J, J_f\right)\beta_{21} - \frac{1}{2}\left(2-3m_r^2\right)\left(\left[a_{22}(\chi_d = 0) + a_{22}(\chi_d = \pi/2)\right]\beta_{22}\right.$$

$$\left.\left.+\left[a_{23}(\chi_d = 0) + a_{23}(\chi_d = \pi/2)\right]\beta_{23}\right) f_2\left(J, J_f\right)\right\}. \tag{20b}$$

On comparing, we find that the ratio (20a) not only contains one additional parameter, but is also more complicated than (19). It is therefore simpler as well as physically more transparent to study unnormalized LD (19) with respect to fluorescence than the degree (20) of LP of radiation emitted in a PEFCO experiment.

In the remaining part of this sub-section, some of the important properties of LD (19) are discussed :

(i) We know from eq. (A2) that $f_2\left(J, J_f\right) = 0$ for $J < 1$. Hence for LD with respect to

fluorescence in PEFCO spectroscopy to exist, the total angular momentum J of the excited photoion AB^{+*} must be greater than 1/2.

(ii) Unlike in the non-coincident FS eq. (2), the LD (19) exists even for $\theta_d = 0$ or π and/ or $\gamma_d = (2n+1)\pi/4$.

(iii) One can readily verify from eqs. (A19)-(A22) that (19) vanishes identically for $\theta_d = 0$ or π plus $\theta_p = 0$ or π. That is, there is no LD if both photoelectron and fluorescence are detected parallel or antiparallel to the Z-axis.

(iv) The parameter α_2 present in (19) can be extracted by measuring along magic angle $\left(\theta_d = 37.5^0\right)$ the intensity of LP fluorescence in a non-coincident experiment performed with LP incident radiation. Here, one should have the angle $\gamma_d \neq (2n+1)$ with $n = 0 - 3$.

(v) One of the simplest geometries to determine parameters β_2, β_{21}, β_{22} and β_{23} present in (19) consists of both the photoelectron and fluorescence detectors in the same plane *i.e.*, $\phi_d - \phi_p = n\pi$ with $n = 0 - 2$. If the fluorescence is observed along Z-axis (*i.e.*, $\theta_d = 0$), expression (19) reduces to

$$\left.\frac{d^2\sigma_{LD}(m_r)}{d\hat{k}_p d\omega_d}\right|_{\phi_d-\phi_p=n\pi}^{\theta_d=0} \equiv \frac{d^2\sigma_{LD}(m_r)}{d\theta_p d\gamma_d} = -\frac{I_0\sigma_p}{4\pi}\sqrt{\frac{5}{6}}\left\{\frac{1}{3}\beta_2 P_2^2(\cos\theta_p)\cos 2\gamma_d\right.$$

$$+\frac{1}{2}m_r\beta_{21}P_2^2(\cos\theta_p)\sin 2\gamma_d + \frac{1}{2}\left(2-3m_r^2\right)\left[\frac{5}{\sqrt{21}}\beta_{22}P_2^2(\cos\theta_p)\right.$$

$$\left.\left.-\frac{1}{2}\sqrt{\frac{3}{7}}\beta_{23}P_4^2(\cos\theta_p)\right]\cos 2\gamma_d\right\} f_2(J, J_f). \qquad (21)$$

If the photoelectron is detected in the X-Y plane (*i.e.*, $\theta_p = \pi/2$), then

$$\left.\frac{d^2\sigma_{LD}(m_r)}{d\theta_p d\gamma_d}\right|_{\theta_p=\pi/2} = -\frac{I_0\sigma_p}{4\pi}\sqrt{\frac{5}{6}}\left[\beta_2\cos 2\gamma_d + \frac{3}{2}m_r\beta_{21}\sin 2\gamma_d\right.$$

$$\left.+\frac{1}{2}\left(2-3m_r^2\right)5\sqrt{\frac{3}{7}}\beta_{22}\cos 2\gamma_d\right] f_2(J, J_f). \qquad (22)$$

This expression can be used to obtain β_{21} if $\gamma_d = (2n+1)\pi/4$ and the absorbed photon is CP (*i.e.* $m_r = \pm 1$). In order to determine β_2 and β_{22}, two more measurement of (22) need to be made taking two different values of γ_d and such that $cos2\gamma_d \neq 0$. These measurements should be performed, preferably, with LP incident radiation. The remaining parameter β_{23} occurring in (19) can be determined by taking in (21) $m_r = 0$, $\theta_p \neq 0$ or $\pi/2$ and $\gamma_d \neq (2n+1)\pi/4$. In this way all the five parameters needed in the complete specification of LD (19) with respect to fluorescence in a PEFCO spectroscopy are extracted from experimental

measurements. Expression (21) and (22) show, in addition, that LD with respect to fluorescence in a PEFCO experiment does not necessarily vanish even in a coplanar experimental arrangement.

4. Application

In this section, we present an application of the frame-work developed in the Section 3. Without doing any dynamical calculations, we derived hereunder explicit expressions for the parameters $\left(\sigma_p, \beta_p, \alpha_1, \alpha_2, \beta_{11}, \beta_{12}, \beta_2, \beta_{21}, \beta_{22}, \beta_{23}\right)$ needed to study CD as well as LD with respect to a photon either absorbed or emitted in a PEFCO experiment. These expressions will be applicable to any linear molecule rotating according to Hund's coupling scheme either (a) and (b).

Let us take total angular momenta J_0 of AB and J of AB^{+*} to be 0 and 1/2, respectively. The corresponding electronic states of AB are [5] then $^{(1,3,5\ )}\Sigma$, $^{(3,5,7\ )}\Pi$, $^{(5,7,9\ )}\Delta$, *etc.*, in Hund's coupling scheme (a) ; $^1\Sigma$, $^3(\Sigma, \Pi)$, $^5(\Sigma, \Pi, \Delta)$, $^7(\Sigma, \Pi, \Delta)$, *etc.* for $N_0 = 0,1,2,3$, *etc.*, in scheme (b), respectively. Here, and in the following, all the symbols have their usual meanings explained elsewhere [5, 24]. Similarly, the possible electronic states of AB^{+*} which will have $J = 1/2$ are $^{(2,4\ )}\Sigma$, $^{(2,4\ )}\Pi$, $^{(4,6\ )}\Delta$, $^{(6,8\ )}\phi$, *etc.* in case (a) ; $^2\Sigma$ for $N = 0$, $^2(\Sigma, \Pi)$ and $^4(\Sigma, \Pi)$ for $N = 1$, $^4(\Sigma, \Pi, \Delta)$ and $^6(\Sigma, \Pi, \Delta)$ for $N = 2$ *etc.* in the Hund's scheme (b).

We know that for $J_0 = 0 \rightarrow J = 1/2$ Photoionizing transition (3a), the only partial waves which can be used to represent a photoelectron are $s\left(l_p = 0\right)$, $p\left(l_p = 1\right)$ and $d\left(l_p = 2\right)$. Due to the parity selection rule (I, A5) applicable in Hund's case (a) or (I.B3) suitable for the case (b), the photoelectron will be represented by either even or odd partial waves. Consequently, each dichoric spectrum in a PEFCO experiment will split in two parts. The gerade part will consist of $\left(l_p = 2, j_p = 1/2\right)$ and $\left(l_p = 2, j_p = 3/2\right)$; whereas the ungerade part will be composed of a single partial wave $l_p = 1$ with $j_p = 1/2, 3/2$. With these values of the various quantum numbers, one can calculated both for gerade and ungerade parts the ten parameters $\left(\sigma_p, \beta_p, \alpha_1, \alpha_2, \beta_{11}, \beta_{12}, \beta_2, \beta_{21}, \beta_{22}, \beta_{23}\right)$ needed to study CD as well as LD in PEFCO spectroscopy discussed in the Section 3 of this paper. However, since $J = 1/2$ in the present application, we find from the respective eqs. (A12), (A15) – (A18) that

$$\alpha_2, \beta_2, \beta_{21}, \beta_{22}, \beta_{23} = 0 \tag{23a}$$

Further, we have

$$f_1\left(J = \frac{1}{2}, J_f = \frac{1}{2}\right) = 4,\ f_1\left(J = \frac{1}{2}, J_f = \frac{3}{2}\right) = -2 \tag{23b}$$

and

$$f_2\left(J = \frac{1}{2}, J_f\right) = 0 \tag{23c}$$

from respective eqs. (A1) and (A2). These values of $f_1\left(J, J_f\right)$ and $f_2\left(J, J_f\right)$ will be valid for the following gerade as well as ungerade parts as long as neither J_0 nor J is changed.

(i) $(l_p, j_p) = \left(0, \frac{1}{2}\right), \left(2, \frac{3}{2}\right)$

The respective eqs. (A9), (A11), (A13), and (A14) give

$$\sigma_p = \frac{K_p}{12}\left(1+\frac{1}{10}\rho_e^2\right)\left|\left\langle \frac{1}{2}; 0\frac{1}{2}\left| F\left(\frac{1}{2}\right)\right| 01\right\rangle\right|^2, \tag{24a}$$

$$\alpha_1 = \frac{1}{4}\frac{1-\frac{1}{20}\rho_e^2}{1+\frac{1}{10}\rho_e^2}, \tag{24b}$$

$$\beta_{11} = \frac{1}{4\sqrt{5}}\frac{\left(\frac{\rho_e^2}{14\sqrt{5}} + \rho_e \cos\Delta_e\right)}{1+\frac{1}{10}\rho_e^2}, \tag{24c}$$

and

$$\beta_{12} = \frac{1}{4\sqrt{5}}\frac{\rho_e \sin\Delta_e}{1+\frac{!}{10}\rho_e^2}. \tag{24d}$$

Here

$$\rho_e = \left|\left\langle \frac{1}{2}; 2\frac{3}{2}\left| F\left(\frac{1}{2}\right)\right| 01\right\rangle\right| \Big/ \left|\left\langle \frac{1}{2}; 0\frac{1}{2}\left| F\left(\frac{1}{2}\right)\right| 01\right\rangle\right| \tag{25a}$$

and

$$\Delta_e = arg\left(\left\langle \frac{1}{2}; 0\frac{1}{2}\left| F\left(\frac{1}{2}\right)\right| 01\right\rangle\right) - arg\left(\left\langle \frac{1}{2}; 2\frac{3}{2}\left| F\left(\frac{1}{2}\right)\right| 01\right\rangle\right). \tag{25b}$$

The E1 photoionization matrix elements $\left\langle J; l_p j_p \left| F(j_t)\right| 01\right\rangle$ used in (25) are defined in eq. (I.A4) for Hund's scheme (a) and in eq. (I. B3) for the scheme (b). Relations (24) show that both magnitudes as well as phases of these amplitudes contribute to a given process. The parameter β_{12} obviously vanishes if the difference (25b) between the phases of two amplitude is $\pm n\pi$ with n an integer. Substitution of (24a-c) in (9) will give CD with respect to the absorbed photon ; whereas all the four parameters (σ_p, α_1, β_{11}, β_{12}) are needed to calculate CD (14) with respect to fluorescence. However, as already explained elsewhere in this paper, there is no LD with respect to the fluorescence because the excited photoion AB^{+*} has total angular momentum $J = 1/2$.

The expression (24a-d) are obviously exact, no approximations are made in their derivations. Consequently the CD's in a PEFCO spectrum obtained using (24a-d) will also be accurate to the same extent to which the dynamical calculations have been performed to

determine ρ_e and Δ_e from eq. (25). Alternatively, one can extract ρ_e and Δ_e from the measurements of the gerade part of CD either with respect to the absorbed or with respect to the emitted photon. The three quantities, namely the magnitudes $\left|\left\langle \frac{1}{2}; 0\frac{1}{2} \middle| F\left(\frac{1}{2}\right) \middle| 01 \right\rangle\right|$ and $\left|\left\langle \frac{1}{2}; 2\frac{3}{2} \middle| F\left(\frac{1}{2}\right) \middle| 01 \right\rangle\right|$ of the E1 matrix elements and the difference Δ_e between their phases are sufficient to completely characterize this part of a PEFCO spectrum.

(ii) $\left(l_p, j_p\right) = \left(1, \frac{1}{2}\right), \left(1, \frac{3}{2}\right)$

For the CD's in the ungerade part of a PEFCO spectrum we find from eqs. (A9), (A11), (A13), and (A14) that

$$\sigma_p = \frac{K_p}{12}\left(2+\rho_0^2\right)\left|\left\langle \frac{1}{2}; 1\frac{1}{2} \middle| F\left(\frac{1}{2}\right) \middle| 01 \right\rangle\right|^2, \tag{26a}$$

$$\alpha_1 = \frac{1}{12\left(2+\rho_0^2\right)}\left(1-\frac{1}{4}\rho_0^2\right), \tag{26b}$$

$$\beta_{11} = \frac{1}{24\left(2+\rho_0^2\right)}\left(\rho_0^2+2\rho_0\cos\Delta_0\right), \tag{26c}$$

and

$$\beta_{12} = \frac{\rho_0 \sin\Delta_0}{12\left(2+\rho_0^2\right)} \tag{26d}$$

respectively. These relations use the definitions

$$\rho_0 = \left|\left\langle \frac{1}{2}; 1\frac{3}{2} \middle| F\left(\frac{1}{2}\right) \middle| 01 \right\rangle\right| \Big/ \left|\left\langle \frac{1}{2}; 1\frac{1}{2} \middle| F\left(\frac{1}{2}\right) \middle| 01 \right\rangle\right| \tag{27a}$$

and

$$\Delta_0 = arg\left(\left\langle \frac{1}{2}; 1\frac{1}{2} \middle| F\left(\frac{1}{2}\right) \middle| 01 \right\rangle\right) - arg\left(\left\langle \frac{1}{2}; 1\frac{3}{2} \middle| F\left(\frac{1}{2}\right) \middle| 01 \right\rangle\right). \tag{27b}$$

Thus two quantities, the ratio ρ_0 of the two amplitudes and difference Δ_0 between their phases are sufficient to determine parameters α_1, β_{11}, β_{12}. However, in order to know the value of σ_p one needs to have also the magnitude $\left|\left\langle \frac{1}{2}; 1\frac{3}{2} \middle| F\left(\frac{1}{2}\right) \middle| 01 \right\rangle\right|$. This much of information is sufficient to completely characterize dichroic effects in the ungerade part of the PEFCO spectrum in the present example. Substitution of (26a-c) in eqs. (9) and of (26a-d) in (19) will completely characterize the CD spectra with respect to the absorbed and emitted photons respectively.

5. Conclusion

Expressions for dichoric affects in PEFCO spectroscopy have been derived for linear molecules rotating according to the Hund's coupling scheme either (a) or (b). The general structure of these expressions is identical in the two coupling schemes. With respect to the absorbed photon, only CD has been studied ; whereas with respect to the fluorescence, both CD and LD have been investigated. The latter two are the unnormalized degrees of circular and linear polarization of fluorescence, respectively. From a theoretical point of view, the study of dichroic effects with respect to fluorescence is found to be much convenient as it involves less number of parameters than degree of its polarization.

The properties of dichoric effects found in a PEFCO spectrum herein are either new or different from those known to exist in noncoincident photoecletron or fluorescence spectra observed separately. Such studies also facilitate the extraction of theoretical parameters from experimental measurements. These parameters are needed in the 'complete' quantum mechanical characterization of a PEFCO spectrum, providing more detailed information on molecular structure.

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Appendix A

In this appendix, we present expressions for the two factors $f_1(J,J_f)$ and $f_2(J,J_f)$, six geometrical constants (a_{11}, a_{12}, a_2, a_{21}, a_{22}, a_{23}) and ten parameters (σ_p, β_p, α_1, α_2, β_{11}, β_{12}, β_2, β_{21}, β_{22}, β_{23}) needed to completely characterize the PEFCO spectrum (8) consisting of spinunresolved angular photocurrent plus polarized fluorescence :

$$f_1(J,J_f)=(-1)^{J-J_f}6(2J+1)\begin{Bmatrix}1 & 1 & 1\\ J & J & J_f\end{Bmatrix}=\sqrt{\frac{3(2J+1)}{2J(J+1)}}\left[J(J+1)-J_f(J_f+1)+2\right] \quad \text{(A1)}$$

$$f_2(J,J_f)=(-1)^{-J-J_f}6(2J+1)\begin{Bmatrix}1 & 1 & 2\\ J & J & J_f\end{Bmatrix}=-\sqrt{\frac{3(2J+1)}{10(2J-1)J(J+1)(2J+3)}}$$

$$\left\{3\left[J(J+1)-J_f(J_f+1)+2\right]\left[J(J+1)-J_f(J_f+1)+1\right]-8J(J+1)\right\} \quad \text{(A2)}$$

$$a_{11}=\left[P_2(\cos\theta_p)\cos\theta_d+\frac{1}{2}P_2^1(\cos\theta_p)\sin\theta_d\cos(\phi_d-\phi_p)\sin2\chi_d\right] \quad \text{(A3)}$$

$$a_{12}=P_2^1(\cos\theta_p)\sin\theta_d\sin(\phi_d-\phi_p)\sin2\chi_d \quad \text{(A4)}$$

$$a_2=\frac{1}{3}\sqrt{\frac{5}{6}}\left\{\left[P_2(\cos\theta_d)-\frac{3}{2}\sin^2\theta_d\cos2\gamma_d\cos2\chi_d\right]P_2(\cos\theta_p)\right.$$

$$+\left[\frac{1}{2}(1+\cos2\gamma_d\cos2\chi_d)\sin2\theta_d\cos(\phi_d-\phi_p)-\sin\theta_d\sin2\gamma_d\sin(\phi_d-\phi_p)\right.$$

$$\left.\cos2\chi_d\right]P_2^1(\cos\theta_p)+\frac{1}{2}\left[\frac{1}{2}\sin^2\theta_d\cos2(\phi_d-\phi_p)-\left(\cos^4\frac{1}{2}\theta_d\cos2(\phi_d-\phi_p+\gamma_d)\right.\right.$$

$$\left.\left.+\sin^4\frac{1}{2}\theta_d\cos2(\phi_d-\phi_p-\gamma_d)\right)\cos2\chi_d\right]P_2^2(\cos\theta_p)\Bigg\} \quad \text{(A5)}$$

$$a_{21}=\frac{5}{4\sqrt{6}}\left\{\left[\frac{1}{2}\left(1+\cos 2\gamma_d\cos 2\chi_d\right)\sin 2\theta_d\sin\left(\phi_d-\phi_p\right)+\sin\theta_d\sin 2\gamma_d\right.\right.$$

$$\left.\cos\left(\phi_d-\phi_p\right)\cos 2\chi_d\right]P_2^1\left(\cos\theta_p\right)+\frac{1}{2}\left[\frac{1}{2}\sin^2\theta_d\sin 2\left(\phi_d-\phi_p\right)-\left(\cos^4\frac{1}{2}\theta_d\right.\right.$$

$$\left.\left.\left.\sin 2\left(\phi_d-\phi_p+\gamma_d\right)+\sin^4\frac{1}{2}\theta_d\sin 2\left(\phi_d-\phi_p-\gamma_d\right)\right)\cos 2\chi_d\right]P_2^2\left(\cos\theta_p\right)\right\} \quad \text{(A6)}$$

$$a_{22}=\frac{5}{6}\sqrt{\frac{5}{14}}\left\{2\left[P_2\left(\cos\theta_d\right)-\frac{3}{2}\sin^2\theta_d\cos 2\gamma_d\cos 2\chi_d\right]P_2\left(\cos\theta_p\right)\right.$$

$$+\left[\frac{1}{2}\left(1+\cos 2\gamma_d\cos 2\chi_d\right)\sin 2\theta_d\cos\left(\phi_d-\phi_p\right)-\frac{1}{2}\sin\theta_d\sin\left(\phi_d-\phi_p\right)\sin 2\gamma_d\cos 2\chi_d\right]$$

$$P_2^1\left(\cos\theta_p\right)-\left[\frac{1}{2}\sin^2\theta_d\cos 2\left(\phi_d-\phi_p\right)-\left(\cos^4\frac{1}{2}\theta_d\cos 2\left(\phi_d-\phi_p+\gamma_d\right)\right.\right.$$

$$\left.\left.+\sin^4\frac{1}{2}\theta_d\cos 2\left(\phi_d-\phi_p-\gamma_d\right)\right)\cos 2\chi_d\right]P_2^2\left(\cos\theta_p\right)\Big\} \quad \text{(A7)}$$

$$a_{23}=3\sqrt{\frac{5}{14}}\left\{\left[P_2\left(\cos\theta_d\right)-\frac{3}{2}\sin^2\theta_d\cos 2\gamma_d\cos 2\chi_d\right]P_4\left(\cos\theta_p\right)+\frac{1}{2}\left[\frac{1}{2}\left(1+\cos 2\gamma_d\cos 2\chi_d\right)\right.\right.$$

$$\left.\sin 2\theta_d\cos\left(\phi_d-\phi_p\right)-\sin\theta_d\sin\left(\phi_d-\phi_p\right)\sin 2\gamma_d\cos 2\chi_d\right]P_4^1\left(\cos\theta_p\right)$$

$$+\frac{1}{12}\left[\frac{1}{2}\sin^2\theta_d\cos 2\left(\phi_d-\phi_p\right)-\left(\cos^4\frac{1}{2}\theta_d\cos 2\left(\phi_d-\phi_p+\gamma_d\right)\right.\right.$$

$$\left.\left.\left.+\sin^4\frac{1}{2}\theta_d\cos 2\left(\phi_d-\phi_p-\gamma_d\right)\right)\cos 2\chi_d\right]P_4^2\left(\cos\theta_p\right)\right\} \quad \text{(A8)}$$

$$\sigma_p=\frac{K_p}{3}\sum_{l_pJ_pJ_t}\left[\left(2l_p+1\right)\left(2j_p+1\right)\left(2j_t+1\right)\right]^{-1}\left|\left\langle J;l_pj_p\left|F(j_t)\right|J_0;1\right\rangle\right|^2 \quad \text{(A9)}$$

$$\beta_p=-\frac{2K_p}{\sigma_p}\sqrt{-\frac{5}{6}}\sum_{\substack{l_pl_p'\\ j_pj_p'J_t}}(-1)^{l_p+l_p'-l_t}\left(2j_t+1\right)^{-1}\begin{pmatrix}l_p & l_p' & 2\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}1 & 1 & 2\\ j_p & j_p' & j_p\end{Bmatrix}\begin{Bmatrix}l_p & l_p' & 2\\ j_p' & j_p & \frac{1}{2}\end{Bmatrix}$$

$$\left\langle J;l_pj_p\left|F(j_t)\right|J_0;1\right\rangle\left\langle J;l_p'j_p'\left|F(j_t)\right|J_0;1\right\rangle^* \quad \text{(A10)}$$

$$\alpha_1 = (-1)^{J+J_0}\frac{K_p}{4\sigma_p}\sum_{\substack{l_p j_p \\ j_t j_t'}}(-1)^{j_p}\left[(2l_p+1)(2j_p+1)\right]^{-1}\begin{Bmatrix}1 & 1 & 1\\ j_t & j_t' & j_p\end{Bmatrix}\begin{Bmatrix}J & J & 1\\ j_t & j_t' & J_0\end{Bmatrix}$$

$$\left\langle J;l_p j_p\middle|F(j_t)\middle|J_0;1\right\rangle\left\langle J;l_p j_p\middle|F(j_t')\middle|J_0;1\right\rangle^* \tag{A11}$$

$$\alpha_2 = (-1)^{J+J_0}\frac{K_p}{6\sigma_p}\sum_{\substack{l_p J_p \\ J_t J_t'}}(-1)^{J_p}\left[(2l_p+1)(2j_p+1)\right]^{-1}\begin{Bmatrix}1 & 1 & 2\\ j_t & j_t' & j_p\end{Bmatrix}\begin{pmatrix}J & J & 2\\ j_t & j_t' & J_0\end{pmatrix}$$

$$\left\langle J;l_p j_p\middle|F(j_t)\middle|J_0;1\right\rangle\left\langle J;l_p j_p\middle|F(j_t')\middle|J_0;1\right\rangle^* \tag{A12}$$

$$\beta_{11} = (-1)^{J_0+J+\frac{1}{2}}\sqrt{\frac{15}{2}}\frac{K_p}{2\sigma_p}\sum_{\substack{l_p l_p' l_t \\ l_p' j_p' j_t'}}(-1)^{l_p'+j_t'}\begin{pmatrix}l_p & l_p' & 2\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}l_p & l_p' & 2\\ j_p' & j_p & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}J & J & 1\\ j_t & j_t' & J_0\end{Bmatrix}$$

$$\begin{Bmatrix}j_p & j_p' & 2\\ j_t & j_t' & 1\\ 1 & 1 & 1\end{Bmatrix}\left\langle J;l_p j_p\middle|F(j_t)\middle|J_0;1\right\rangle\left\langle J;l_p' j_p'\middle|F(j_t')\middle|J_0;1\right\rangle^* \tag{A13}$$

$$\beta_{12} = i(-1)^{J_0+J+\frac{1}{2}}\frac{5K_p}{2\sigma_p\sqrt{6}}\sum_{\substack{l_p l_p' l_t \\ l_p' j_p' j_t'}}(-1)^{j_p'+j_t'}\begin{pmatrix}l_p & l_p' & 2\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}l_p & l_p' & 2\\ j_p' & j_p & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}J & J & 1\\ j_t' & j_t & J_0\end{Bmatrix}$$

$$\begin{Bmatrix}j_p & j_p' & 2\\ j_t & j_t' & 1\\ 1 & 1 & 2\end{Bmatrix}\left\langle J;l_p j_p\middle|F(j_t)\middle|J_0;1\right\rangle\left\langle J;l_p' j_p'\middle|F(j_t')\middle|J_0;1\right\rangle^* \tag{A14}$$

$$\beta_2 = -(-1)^{\frac{1}{2}+J+J_0}\frac{K_p}{2\sigma_p}\sum_{\substack{l_p j_p j_t \\ l_p' j_p' j_t'}}(-1)^{j_t+j_t'}\begin{pmatrix}l_p & l_p' & 2\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}l_p & l_p' & 2\\ j_p' & j_p & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}J & J & 2\\ j_t & j_t' & J_0\end{Bmatrix}$$

$$\begin{Bmatrix}j_p & j_p' & 2\\ j_t' & j_t & 1\end{Bmatrix}\left\langle J;l_p j_p\middle|F(j_t)\middle|J_0;1\right\rangle\left\langle J;l_p' j_p'\middle|F(j_t')\middle|J_0;1\right\rangle^* \tag{A15}$$

$$\beta_{21} = i(-1)^{\frac{1}{2}+J_0+J} \frac{K_p}{\sigma_p} \sum_{\substack{l_p l_p' l_t \\ l_p' l_p' l_t'}} (-1)^{l_p'+l_t'} \begin{pmatrix} l_p & l_p' & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_p & l_p' & 2 \\ j_p' & j_p & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} J & J & 2 \\ j_t' & j_t & J_0 \end{Bmatrix}$$

$$\begin{Bmatrix} j_p & j_p' & 2 \\ j_t & j_t' & 2 \\ 1 & 1 & 1 \end{Bmatrix} \langle J; l_p j_p | F(j_t) | J_0; 1 \rangle \langle J; l_p' j_p' | F(j_t') | J_0; 1 \rangle^* \qquad \text{(A16)}$$

$$\beta_{22} = (-1)^{\frac{1}{2}+J_0+J} \frac{K_p}{\sigma_p} \sum_{\substack{l_p l_p' l_t \\ l_p' l_p' l_t'}} (-1)^{l_p'+l_t'} \begin{pmatrix} l_p & l_p' & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_p & l_p' & 2 \\ j_p & j_p' & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} J & J & 2 \\ j_t & j_t' & J_0 \end{Bmatrix}$$

$$\begin{Bmatrix} j_p & j_p' & 2 \\ j_t & j_t' & 2 \\ 1 & 1 & 2 \end{Bmatrix} \langle J; l_p j_p | F(j_t) | J_0; 1 \rangle \langle J; l_p' j_p' | F(j_t') | J_0; 1 \rangle^* \qquad \text{(A17)}$$

$$\beta_{23} = (-1)^{J_0+J-\frac{1}{2}} \frac{K_p}{\sigma_p} \sum_{\substack{l_p l_p' l_t \\ l_p' l_p' l_t'}} (-1)^{l_p'+l_t'} \begin{pmatrix} l_p & l_p' & 4 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_p & l_p' & 4 \\ j_p' & j_p & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} J & J & 2 \\ j_t' & j_t & J_0 \end{Bmatrix}$$

$$\begin{Bmatrix} j_p & j_p' & 4 \\ j_t & j_t' & 2 \\ 1 & 1 & 2 \end{Bmatrix} \langle J; l_p j_p | F(j_t) | J_0; 1 \rangle \langle J; l_p' j_p' | F(j_t') | J_0; 1 \rangle^* \qquad \text{(A18)}$$

In eqs. (A1) and (A2), J and J_f are respectively the total angular momenta of the excited photoion AB^{+*} and of the residual ion AB^+ formed in the process (3). In eqs. (A3) – (A8), (θ_p, ϕ_p) are the spherical angles of the photoelectron propagation vector $\boldsymbol{k}_p$ in the space-frame OXYZ, $\omega_d(\phi_d, \theta_d, \gamma_d)$ are the Euler angles of the fluorescence detector-frame $OX_dY_dZ_d$ with respect to the OXYZ coordinate system, and angle χ_d specifies polarization vector $\hat{\varepsilon}_d$ $(\cos\chi_d, i\sin\chi_d, 0)$ of the fluorescence in its own (*i.e.*, $OX_dY_dZ_d$) frame. In eqs. (A9)-(A18), constant $K_p = 3\pi(e^2/\alpha_0 E_0)^2$ with α_0 the dimensionless fine structure constant and $E_0 = h\nu_0$ the energy of the photon absorbed in (3a). The photoionization matrix elements used in (A9)-(A18) are taken from eqs. (I.A4) and (I.B2) for Hund's coupling schemes (a) and (b), respectively.

In (19) and the subsequent equations in the sub-section 3.3., we have used coefficients b_2, b_{21}, b_{22} and b_{23}. The detailed expressions for these coefficients are as follows :

$$b_2 = a_2(\chi_d = 0) - a_2(\chi_d = \pi/2)$$

$$= \frac{1}{3}\sqrt{\frac{5}{6}}\left\{\left(2\left[\cos\theta_d \cos 2\gamma_d \cos(\phi_d - \phi_p) - \sin 2\gamma_d \sin(\phi_d - \phi_p)\right]P_2^1(\cos\theta_p)\right.\right.$$

$$\left. -3\sin\theta_d \cos 2\gamma_d \times P_2(\cos\theta_p)\right)\sin\theta_d - \left[\cos^4\frac{\theta_d}{2}\cos 2(\phi_d - \phi_p + \gamma_d)\right.$$

$$\left.\left. +\sin^4\frac{1}{2}\theta_d \cos 2(\phi_d - \phi_p - \gamma_d)P_2^2(\cos\theta_p)\right]\right\}. \tag{A19}$$

$$b_{21} \equiv a_{21}(\chi_d = 0) - a_{21}(\chi_d = \pi/2)$$

$$= \frac{5}{2\sqrt{6}}\left\{\left[\sin 2\gamma_d \cos(\phi_d - \phi_p) + \cos\theta_d \cos 2\gamma_d \sin(\phi_d - \phi_p)\right]\sin\theta_d P_2^1(\cos\theta_p)\right.$$

$$\left.-\left[\cos^4\frac{1}{2}\theta_d \sin 2(\phi_d - \phi_p + \gamma_d) + \sin^4\frac{1}{2}\theta_d \sin 2(\phi_d - \phi_p - \gamma_d)P_2^2(\cos\theta_p)\right]\right\}, \tag{A20}$$

$$b_{22} \equiv a_{22}(\chi_d = 0) - a_{22}(\chi_d = \pi/2)$$

$$= \frac{5}{3}\sqrt{\frac{5}{14}}\left\{\left(\left[\cos\theta_d \cos 2\gamma_d \cos(\phi_d - \phi_p) - \frac{1}{2}\sin 2\gamma_d \sin(\phi_d - \phi_p)\right]P_2^1(\cos\theta_p)\right.\right.$$

$$\left. -3\sin\theta_d \cos 2\gamma_d P_2(\cos\theta_p)\right)\sin\theta_d + \left[\cos^4\frac{1}{2}\theta_d \cos 2(\phi_d - \phi_p + \gamma_d)\right.$$

$$\left.\left. +\sin^4\frac{1}{2}\theta_d \cos 2(\phi_d - \phi_p - \gamma_d)\right]P_2^2(\cos\theta_p)\right\}. \tag{A21}$$

$$b_{23} \equiv a_{23}(\chi_d = 0) - a_{23}(\chi_d = \pi/2)$$

$$= 3\sqrt{\frac{5}{14}}\left\{\left(\left[\cos\theta_d \cos 2\gamma_d \cos(\phi_d - \phi_p) - \sin 2\gamma_d \sin(\phi_d - \phi_p)\right]P_4^1(\cos\theta_p)\right.\right.$$

$$\left. -3\sin\theta_d \cos 2\gamma_d P_4(\cos\theta_p)\right)\sin\theta_d - \frac{1}{6}\left[\cos^4\frac{1}{2}\theta_d \cos 2(\phi_d - \phi_p + \gamma_d)\right.$$

$$\left.\left. +\sin^4\frac{1}{2}\theta_d \cos 2(\phi_d - \phi_p - \gamma_d)P_4^2(\cos\theta_p)\right]\right\}. \tag{A22}$$

These relation are readily obtained using the respective eqs. (A5)-(A8).